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Rational design of bimetallic nanocatalysts for tandem transformations

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Abstract

Tandem reactions consist of a sequence of two or more distinct transformations that can be achieved in a single synthetic step. A new article by Sun and colleagues (Matter, 2019) demonstrates how the catalytic properties of bimetallic nanoparticles can be rationally optimized to enable the one-pot synthesis of polybenzoxazole (PBO).

Keywords: nanocatalysis; bimetallic nanoparticles; tandem reactions; controlled polymerization

Tandem reactions involve two or more distinct molecular transformations in a single step without the need for intermittent work-up and purifications, fitting perfectly into the Principles of Green Chemistry [1,2]. The ability to carry out tandem reactions using nanoparticle catalysts that can display selectivity while also being recoverable and reusable is a significant challenge for the sustainable production of chemicals.

Recent advances in the synthesis and characterization of bimetallic nanoparticles (NPs) has enabled scientists to establish more precise structure-performance relationships in catalysis. This knowledge has provided the foundation for understanding how the NP physiochemical properties (e.g., size, shape, and composition) affect catalytic performance in terms of conversion percentages and reaction selectivity [3]. This, in turn, has been fundamental for a transition to a design-driven approach in catalysis, where the NP physiochemical features can be tailored via rational design based on a target transformation [4].

One remarkable example of this approach involves the development of nanocatalysts for the dehydrogenation of formic acid (FA) (i.e., $HCOOH \rightarrow CO_2 + H_2$) [5-7]. It has been established that Pd-based catalysts display the best performance in this transformation. In this case, surface electronic density, surface tension, and atomic arrangements are central to the catalyst activity and selectivity [6,7]. In fact, many of the Pd-based nanocatalysts properties exhibit a volcano-type relationship between activities for the formic acid dehydrogenation and composition, for example. In this case, activity as a function of composition passes through a maximum in a region of ideal compositions, where the interaction between the surface and the substrate are optimized and the plot of reaction rates as a function of composition resembles the shape of a triangle or volcano, following the Sabatier principle. These relations have been widely exploited to rationally design bimetallic NPs with optimized catalytic performances. However, these studies have traditionally focused on single-step reactions. An expansion for tandem transformations is significantly more challenging because two or more reactions can be affected differently by the changes in the physiochemical properties of the bimetallic catalyst.

In a recent manuscript published in *Matter* [8], Sun and collaborators demonstrated the development of bimetallic AuPd NPs as catalysts for tandem reactions that include FA dehydrogenation, nitro-hydrogenation, and amine/aldehyde condensation to produce the important polymer polybenzoxazole (PBO). The authors systematically investigated AuPd NPs of varying composition (Au, $Au_{70}Pd_{30}$, $Au_{61}Pd_{39}$, $Au_{53}Pd_{47}$, $Au_{39}Pd_{61}$, $Au_{28}Pd_{72}$, and Pd) and size (4, 6, 8, and 10 nm) for each step, and unraveled how the performance for the one-pot reaction depends on both AuPd NP size and composition. Once the reaction starts via FA dehydrogenation, it was expected that the catalyst activity depends on its surface electronic density, and consequently, the surface composition. In agreement

with previous reports, the $Au_{39}Pd_{61}$ alloy displayed the highest activity for FA dehydrogenation [7]. It was also confirmed that the higher compressive strain of the AuPd NP surface promotes FA dehydrogenation. Thus, smaller NPs showed the highest turnover frequencies for this reaction. In the NO_2 hydrogenation step, it was found that surface compression also decreases the migration of surface H* towards O-NO (the only endothermic step). Therefore, activity increased with decreasing NP size as was observed for the FA dehydrogenation step. For the condensation step, the C-N bond formation was rate-determining and enhanced by surface compression as a result of weakened adsorption of amino and carbonyl groups. Interestingly, it was discovered that larger NPs are required for this step because the condensation involves two large molecules (amine and aldehyde). In this case, smaller NPs cannot properly accommodate the reactants in a safe distance from the under-coordinated edge sites (i.e., poorly selective sites), lowering the reaction activity. Therefore, when the balance of compressive strain and geometric effects were considered, 8 nm NPs displayed the best activities for the polymerization reaction with a volcano-type variation between NPs size and performance (Figure 1).

This study represents an excellent example of using the critical mass of knowledge generated over the years on controlled NP synthesis and structure-performance relationships to achieve optimized catalytic performance in a tandem transformation. In addition to successfully performing a tandem reaction in high yields and under more environmentally friendly conditions to obtain PBO, the reported approach produced PBO with outstanding properties (e.g., improved stability) which is essential for technological application of this polymer.

This paper demonstrates the unraveling and application of design principles to the rational design of bimetallic AuPd NPs to perform a series of reactions in one-pot for the synthesis of an important polymer with optimized catalytic properties. Although this is a remarkable result, to employ this approach for other tandem reactions and NPs systems will require further developments and knowledge on the controlled synthesis of NPs, their precise characterization, and structure-performance relationships. The understanding of these relations for the AuPd NPs for FA dehydrogenation was one of the foundations to make this important study possible. We believe further developments in the understanding and rational design of NPs for tandem reactions hold great promise for extending the field of nanocatalysis beyond the state-of-the-art, allowing for a transition to design-driven and more environmentally friendly processes with less energy consumption, reaction steps, and generation of waste or by-products.

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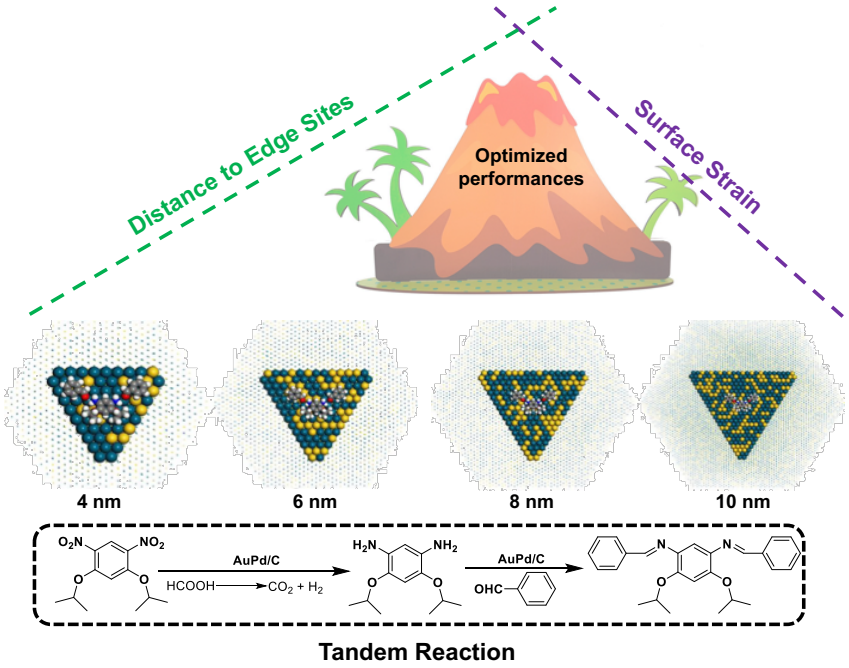

Figure 1. A Balandin's volcano trade-off between activity and size in $Au_{39}Pd_{61}$ NPs for the tandem reaction to produce polybenzoxazole (PBO). The tandem reaction involves formic acid-induced reduction of 1,5-diisopropoxy-2,4-dinitrobenzene, and the subsequent condensation of the 1,5-diisopropoxy-2,4-aminobenzene product with benzaldehyde leading to the formation of small subunits of PBO.